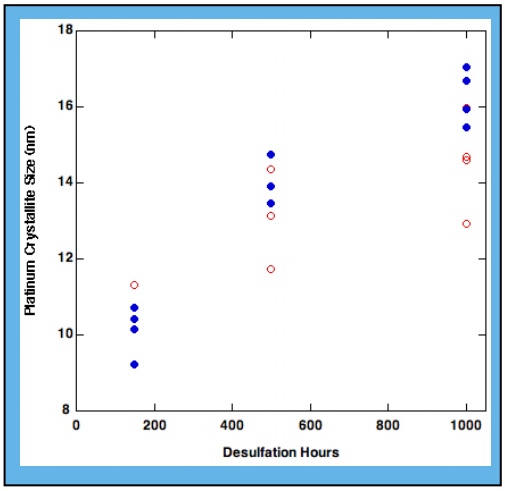
Development of Materials Analysis Tools For Studying NOx Adsorber Catalysts

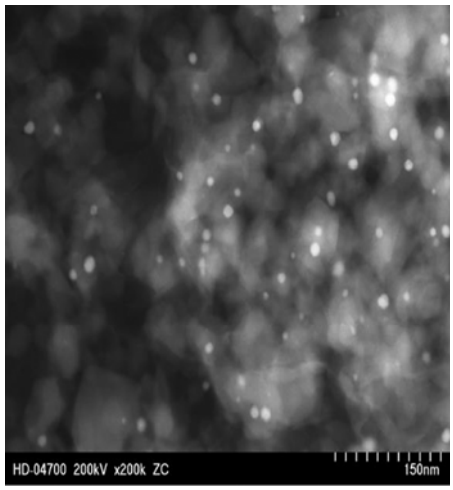
Background

In order to meet the 2007 emission requirements for diesel exhaust, aftertreatment in engines may be necessary. The technology necessary for 2007 will need to integrate aftertreatment with engine control systems. Currently, no commercial off-the-shelf technologies are available to meet these standards. Consequently, Cummins, Inc., is working to understand the basic science necessary to effectively utilize these catalyst systems. The Oak Ridge National Laboratory (ORNL) is assisting with the materials characterization effort.

Base-metal oxides (BMOs) are major components in current oxides of nitrogen (NOx) adsorber catalysts that Cummins seeks to use in aftertreatment systems. Although the function of these adsorbers is to collect surface NOx species, they also collect oxy-sulfur (SOx) species. Both species are to be released from these surface sites during different regenerations, where the adsorber BMO is either heated to some critical temperature and/or exposed to a reducing or reactant atmosphere. Sulfur adsorption is unfortunately a form of poisoning of adsorber catalysts and is a major problem that must be resolved for BMO-based emission reduction technologies to become commercially viable.



Pt atoms begin to sinter as time at desulfation temperature increases



HA-ADF image from the STEM showing Pt particles in bright contrast after 150 desulfation hours

Benefits

- Furthers the fundamental understanding of NOx adsorber catalyst activity
- Assists engine and catalyst manufacturers in meeting 2007 emission requirements for diesel exhaust

The Technology

The crystal structure, morphology, phase distribution, particle size and surface species of catalytically active materials supplied by Cummins will be characterized using X-ray diffraction (XRD), Raman spectroscopy, and electron microscopy. These materials will come from all stages of the catalyst's life cycle: raw materials, as-calcined, sulfated, regenerated, and so forth. Both ORNL and Cummins personnel have participated in this work.

Platinum (Pt) is the catalytically active element which must remain dispersed and of small size within the adsorber. Laboratory-based engine tested samples showed Pt particle growth as a function of desulfation time. XRD showed Pt particle growth using a peak breadth analysis, which agreed with the Raman and microscopy work.

Raman spectroscopy measures the characteristic vibrational energy levels of molecules and crystals and so is very sensitive to any changes in bonding, stoichiometry and phase/symmetry. In this case, frequency changes of a washcoat component vibration were monitored with desulfation time. We discovered a decrease in peak width and the increase in peak position of a washcoat-attributed Raman band, which occurs due to the growth of the Pt particle size. Although Raman spectroscopy could not directly measure the Pt particle size in these samples, the changes in the Raman spectra with Pt size were calibrated for this specific catalyst formulation such that Raman could nondestructively measure Pt particle coarsening.

High-angle annular dark-field (HA-ADF) images taken with scanning transmission electron microscopy (STEM) indicated that samples with 150, 500, and 1000 desulfation hours displayed 8, 9.5, and 10.5 nm Pt particles, respectively, which was consistent with the XRD results. HA-ADF images on the STEM provided a facile method for imaging the particles in high contrast and for measuring particle sizes. Digital processing yielded Pt particle size distributions allowing for statistical analysis.

Where Can I Find More Information?

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